Bonding of Agrofibers-based Composition Panels

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Abstract: Urea formaldehyde resins were formulated with variables of three reaction pHs (1.0, 4.8, and 8.0 - 5.0) and three catalysts (sodium hydroxide, sodium hydroxide/ammonium mix, and triethanolamine) . The resins were prepared by placing all formaldehyde and water in reaction kettle and pH was adjusted with sulfuric acid and sodium hydroxide, respectively. Urea was added in 1.5 equal parts at 1 - minute intervals.

The proportion of high molecular weight products in the rosin increased substantially as the reaction pH decreased. The formation of a high percentage of uron derivatives under strong acidic conditions indicated these resins differed considerable from conventional UF resins formulated in the past.

Bagasse panels bonded with UF resins formulated with acidic pH resulted in higher IB than with those formulated with the conventional alkaline - acidic pH system. Similar results were also shown with PMDI/UF bonded Bagasse panels. The apparently higher IB strength of PMDI/UF resin systems indicate that these resin systems would be expected to provide the greatest potential for further improvement in terms of IB/cost basis. It is noted that mixed catalyst system of sodium hydroxide/ammonium and triethanohunine yielded a higher average IB, while sodium hydroxide catalyst resulted in a lower IB than commercial UF resin used as control. Since the cost of UF is substantially lower than that of PMDI, economic gains of PMDI/UF resin could be significant by using UF resin as the major component in the system.

Keywords: Urea formaldehyde resin, polyisocyanate, internal bond strength, gel permeation chromatography, ^{13}C NMR, Bagasse

INTRODUCTION

Low cost and proven performance has made urea -formaldehyde resins (UF) the most important wood adhesive for interior applications. However, bonding agrofibers with UF was found to be less effective compared with wood bonding (Hse, 2000). In the U. S., most agrofibers panel products on the market today use polyisocyanate (PMDI) as a binder (Bluegrass and burgess plant). While PMDI produces high quality panel products, its high - cost has limited the development of markets the products. Therefore, the development of a cost - effective resin adhesive system for agrofibem is an important research area.

This paper is one of a series describing efforts at the Pineville, Louisiana, Laboratory of the Southern Research Station to develop effective economical multi - polymer adhesive systems encompassing UF' s low cost, phenol formaldehyde (PF) resin' s durability, and PMDI' s reactivity. The research involved the investigation of: (1) UF resin properties as affected by reaction pH, (2) effect of UF resins formulated at three reaction pHs on IB of PMDI/UF bonded bagasse panels, and (3) effects of UF resins formulated with three reaction catalysts on bond performance of PMDI/UF resin adhesive. Other phases of the development are described in the following manuscripts:

- Development of a resin system for gluing southern hardwood flakeboards (Hse 1978)

• Development of an improved adhesive system for southern pine plywood (Hse 1978)

• Method of bonding particleboard and the like using polyisocyanate/ phenolic adhesive (Hse 1980)

• Blending of urea - formaldehyde and phenol - formaldehyde resin adhesives (Hse 1995)

• Modified formaldehyde - based resin adhesives for rice husk/wood particleboard (Hse and Choong 2000)

MATERIALS AND METHODS

RESIN PREPARATION

2All UF resins were prepared in the laboratory. Each resin preparation was replicated one time. To prepare each resin, all formaldehyde and water were placed in a reaction kettle and pH was adjusted with sulfuric acid and sodium hydroxide, respectively. Urea was added in 15 equal parts at 1 - minute intervals. To initiate the reaction, the mixture was heated and maintained at 50℃ for the first 30 minutes; thereafter, temperature was increased to 80℃ with the exception of the resin made at strong acidic condition that was reacted at 60°C. When the viscosity reached Gardner - Holt viscosity A, the reaction was stopped by rapidly cooling the mixture to 25°C. Gel time, pH, solid content, specific gravity, and free formaldehyde were determined. The vriables for resin preparation were:

Reaction pH:

a. Strong acid - pH 1.0

b. Weak acid - pH 4.8

c. Alkaline - acid - pH 8.0 for 30 minutes and then adjusted to 5.0.

Catalyst:

a. Sodium hydroxide

b. Sodium hydroxide/ammonium mix

c. Triethanolamine

Gel - Permeation Chromatography

A Water Associates GPC with for Shodex GPC - AD - 802s columns was used with dimethylforamide solvent at flow rate of 1 ml/minute. This gel is a polystyrene - divinyl benzene copolymer that has an exclusion limit of 8,000 (polystyrene molecular weight).

Sample injection volume was 100 uL at concentration of 1 percent (w/V).

NMR Measurement

Each resin was diluted with 2 - to 3 - volumes of deuterium oxide and a 13C - NMR spectrum was obtained using a FX - 100 spectrometer (Japan Electron Optics Lab. Co.) at a frequency of 25.0 MHz. A 7.0 - sec pulse delay time and a 450 pulse were used with the gated decoupling to remove N. 0. E. Chemical shifts were determined using internal methanol at 50.0 ppm. Quantitative analyses were based on the signal intensities.

Free Formaldehyde Determination

A slightly modified sodium sulfite method was used for determination of free formaldehyde in the resins. Fifty mL of a 1 - molar solution of sodium sulfite and three drops of thymophthalein indicator solution was placed in a 250 mL Erlenmeyer flask and carefully neutralized by titration with hydrochloric acid until the blue color of the indicator disappeared. An accurately measured, neutralized resin sample was then added to the sodium sulfite solution and the temperature was kept at 4 oC to minimize hydrolysis of the resin. The resulting mixture was titrated with the 0. 1 N HCL to complete decoloration. The percent of free formaldehyde was determined as:

$$\% \text{ CHO} = \frac{(\text{acid titer})\ (\text{normality of acid})\ (3.003)}{\text{weight of sample}}$$

Glue Bond Performance

All panels were prepared in the laboratory with dried hagasse fibers obtained at a bagasse panel plant in Louisiana and used without additional preparation. The sieve analysis of particles showed:

+ 8 mesh	2. 5%
- 8 mesh, + 20 mesh	7. 5%
- 20 mesh, + 35 mesh	11.3%
- 35 mesh, + 40 mesh	4.5%
- 40 mesh	77.5%

The UF resins were adjusted to F/U ratio of 1.25/1 by adding urea 24 hours before blending. The components of the PMDI/UF resins were applied separately by sprayer in a rotating drum with air - atomizing nozzles and reacted in situ to form the alloy adhesive system. All PMDI was applied before the UF resin adhesive. The general conditions for board manufacture were:

Panel size: 50 x 60 cm

Particle moisture content: 4.5%

Resin content: 9. 0 % (2% PMDI and 7% UF) for UF resins formulated with various reaction pH, and 8.0% (1% PMDI and 7% UF) for UF resins formulated with various catalysts

Hot press temperature: 190 ℃

Hot press time: 4 minutes

Internal bond (IB) strength was measured in accordance with ASTM standards for evaluating the properties of wood - base fiber and particle panel materials (D - 1037 - 93).

RESULTS AND DISCUSSION

Effects of reaction pH on UF Resin Properties

Average physical and chemical properties of UF resins as affected by reaction pH are summarized as follows:

Reaction pH	F/U ratio	Solid content (%)	Viscosity (cps)	Specific gravity	Free HCHO(%)
1. 0	3. 0	45	80	1. 255	6. 3.5
4. 8	3.0	51	65	1.255	6. 31
8. 0 - 5. 0	3 . 0	51	35	1.246	5. 70

In general, the high free -formaldehyde content of these resins was expected due to the high F/U molar ratio in the resin preparation. It is noted also the free - formaldehyde decreased as the reaction pH increased. This result agreed with the general belief that the addition of formaldehyde is enhanced and the methylol compounds obtained are relatively stable under alkaline conditions as compared to that of acidic conditions. Since strong acidic catalyst was thought to promote higher degrees of condensation of the resins, the viscosity of the resin decreased as the reaction pH increased. Differences in resin specific gravity were not significant.

EFFECT OF REACTION PH ON RESIN STRUCTURE

The effect of reaction pH on resin structure was investigated by 13C - NMR spectroscopy. 13C - NMR spectra of resins prepared at various pH conditions are shown in Figure 1. Each signal observed in the 13C - NMR spectrum could be assigned according to chemical shifts reported earlier (Tomita and Hatano 1978; Slonim et al. 1977; Ebdon and Heaton 1977) . In the 13C - NMR spectra of resins synthesized under strong acid conditions of pH 1.0, the signals attributed to the carbonyl carbons of uron derivatives were evident at 155 - 156 ppm as well as those of urea residues at about 160 ppm. The results of quantitative measurements are summarized in Table 1. The high free formaldehyde content in all resins, caused by the high molar ratio of F/U, was confirmed also with free -formaldehyde determination by sodium sulfite method. The free formaldehyde content decreased with increased reaction pH. A large amount of hemiformal methylol group was evident in resins prepared with higher free - formaldehyde. Methylene linkage between urea residues increased as the pH was lowered, while dimethylene ether linkages increased with increased reaction pH.

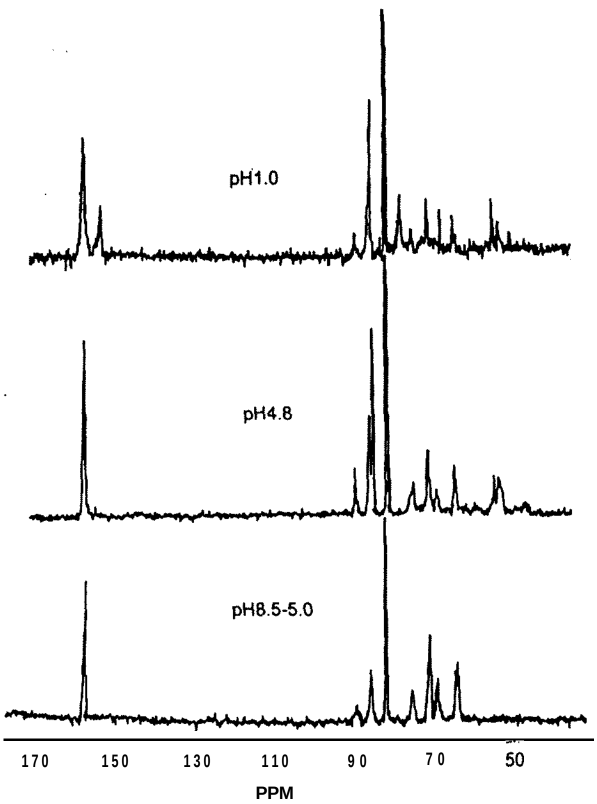

Fig. 1 ^{13}C-NMR spectra of UF resins reacted at various pH conditions at F/U ration of 3/1.

At the strong acidic condition of pH 1.0, however, the greater part of dimethylene ether group was confirmed to be involved in the formation of uron rings. Since two methylene carbons are joined with a carbonyl carbon in the formation of the uron ring, the result indicated that the quantity of methylene carbon incorporated in uron was F/U = 0.5. On the other hand, the quantity of dimethylene ether as determined in Table 1 was F/U = 0.52, which was only slightly higher than the value of 0.5. Since the carbonyl carbon in the uron ring could not be detected in resins made at higher pH, the formation of uron derivatives was indicative of reactions made under strong acid conditions.

GEL PERMEATION CHROMATOGRAPHY

The significant effect of reaction pH on molecular weight distribution is illustrated in Figure 2. The large fraction of sample eluted between 21 and 29 mL indicated that strong acidic conditions favored condensation. On the other hand, the strong signal between 30 and 39 mL showed that alkaline conditions enhanced methylol formation. The high methylol content in resins made under alkaline conditions as compared to acidic conditions was also detected by ^{13}C – NMR analysis (Table 1) . In general, GPC can be divided into two groups of peaks. The peaks between 39 and 40 mL elution volume are those of urea and mono – methylol urea, the first negative peak between 41 and 43 mL is due to formaldehyde and water in the sample. These identifications were made by comparing GPC chromatograms of UF resins before and after addition of urea, formaldehyde, and water to the sample. Other peaks evident at early stages of reaction (i. e., those between elution volumes 30 and 39 mL) may be dimmers trimers and tetramers of polymethylol urea as indicated by previous workers (Dankelman et al. 1976; Dunky and Lederer 1982; Matsuzaki et al. 1980; Tsuge 1980) These peaks can be integrated together (group A) as an estimate of the amount of low molecular weight products. The peaks at low elution volumes (i. e., 21 to 29 mL) can be integrated together (group B) to represent a measure of the high molecular weight products obtained from condensation reactions.

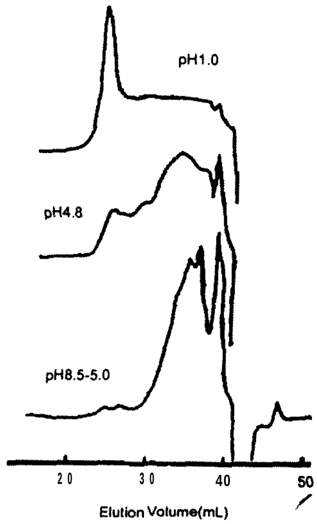

Fig. 2 GPC chromatogram of UF resins reacted at different pH conditions at F/U ratio of 3/1

The composition of low and high molecular weight products are summarized as follows:

Resin	PH	F/U ratio	Low molecular Weight products%	High molecular Weight products%
A	1.0	3.0	54.7	45.3
B	4.8	3.0	79.8	20.2
C	8.0-5.0	3.0	96.2	3.8

The proportion of high molecular weight products increased substantially as the reaction pH decreased. It should be noted, however, the molecular weight buildup for the resin made with pH 1.0 was so fast that controlling reaction temperature was critical in preventing the formation of an insoluble gel in resin preparation.

Gluebond Performance

Effect of reaction pH on internal bond strength

Average internal bond strength cf the bagasse panels are summarized as follows:

Resin	Reaction pH	Resin content (%)	Panel density (g/cm³)	IB (Kpa)
A	1.0	9	0.825	591.6
B	4.8	9	0.817	569.5
C	8.0 – 5.0	9	0.831	461.3
PMDI/A	–	2% PMDI/7% UF	0.820	1224.5
PMDI/B	–	2% PMDI/7% UF	0.831	1173.5
PMDI/C	–	2% PMDI/7% UF	0.811	1126.6
PMDI		4% PMDI	0.763	1012.8

Table 1. ^{13}C – NMR analysis of urea resin sample.

	Reaction pH		
Structure	pH 1	pH 4.8	pH8 5.0
Total methylene	0.63 (20.4)	0.53 (16.9)	0.41 (12.7)
$-NHCH_2NH-$	0.10	0.09	0.14
$-N(CH_2-)CH_2-)2NH-$	0.30	0.32	0.18
$-N(CH_2-)CH_2N(CH_2-)-$	0.23	0.12	0.09
Total methylol	0.93 (30.0)	0.87 (28.3)	1.14 (35.2)
$-NHCH_2OH$	0.19	0.31	0.50
$-NHCH_2OCH_2OH$	0.14		
$-N(CH_2-)CH_2OH$	0.39	0.56	0.64
$-N(CH_2-)CH_2OCH_2OH$	0.21		
Total methylated methylol	0.10 (3.2)	0.05 (1.5)	0
$-NHCH_2OCH_3$	0.10	0.03	
$-N(CH_2-)CH_2OCH_2$		0.02	
Total dimethylene ether	0.52 (17.0)	0.44 (14.0)	0.91 (28.1)
$-NHCH_2OCH_2NH-$	0.13	0.14	0.0
$-N(CH_2-)CH_2OCH_2=$	0.39	0.30	0.41
Total free formaldehyde	0.92 (30.0)	1.22 (39.3)	0.77 (23.9)
$HOCH_2OH$	0.43	0.45	0.25
$HOCH_2OCH_2OH$	BH		
$=NCH_2OCH_2OH$	0.43	0.62	0.41
$HOCH_2OCH_3$ $-CH_2OCH_2OCH_3$	0.06	0.15	0.11
Total carbonyl carbon	1.00	1.00	1.00
$=NCON=$	0.75	1.00	1.00
URON	0.25.		
$H_2NCONHCH_2OH$			
H_2NCONH_2			
Total formaldehyde	3.1 (100)	3.1 (100)	3.2 (100)
Combined formaldehyde	2.18 (70.3)	2.1 (60.7)	2.4 (76.1)

The IB was consistently higher with UF resins formulated with acidic pH than with those formulated with the conventional alkaline - acidic pH system. Similar results were also shown with PMDI/UF bonded bagasse panels. It is noted that 2% PMDI/7% UF resin systems resulted in significantly higher IB than that of 4% PMDI. The results suggest the superiority of the resin system containing PMDI is apparent for all resins in the test. Since the cost of UF (\$0. 15 ~ 0. 17/lb) is substantially lower than that of PMDI (0.75 ~ 0. 85/lb, economic gains of PMDI/UF resin could be substantial by using UF resin as the major component in the system.

Further, the apparently higher IB strengths of PMDI/UF resin systems indicate that these resin systems would be expected to provide the greatest potential for further improvement in terms of IB/cost basis. It should be noted, however that to maintain optimum on IB/cost ratio, the improvement would most likely come from the increase in UF resin level or decrease in PMDI level. Thus, 8% resin content level (1% PMDI/7% UF) was selected for the subsequent evaluations of catalyst effect on IB.

Effect of catalyst on internal bond strength

Average IB of bagasse panels is summarized as follows:

Resin	Catalyst	Resin content(%)	Panel density(g/cm^3)	IB(KPa)
B-1	NaOH	1% PMDI/7% UF	0.785	488.8
B-2	$NaOH/NH_3$	1% PMDI/7% UF	0.764	684.0
B-3	Triethanolamine	1% PMDI/7% UF	0.787	648. 8
UF-C	Commercial	1% PMDI/7% UF	0.775	595.7

Two catalyst systems (mixed catalyst system of NaOH/NH3 and triethanolamine) yielded a higher average IB, while NaOH catalyst resulted in a lower IB than commercial UF resin used as control. Although 1% PMDI resulted in substantially lower IB than that of 2% PMDI in the resin systems, it is noted, however, in this preliminary study that the apparently average IB strength was still higher than the requirements of type 1-M-3 grade of the American Standard of Mat-Formed Particleboard.

CONCLUSIONS

A new adhesive system was obtained by applying minor component of PMDI before the major component of UF resin and then reacting the combined adhesive in situ. The apparent high IB strength indicated that the new resin system is suitable for bonding bagasse fibers and provided the greatest potential for further improvement in terms of IB/cost basis. UF resins formulated with acidic pH and catalyzed with mixed catalyst of NaOH/NH3 were shown to perform best in reacting with PMDI in the combined resin system.

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